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DIELECTRIC LOSSES AND CONDUCTIVITY OF Zr-RICH PZT

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Abstract. The temperature and frequency dependence of the dielectric constant and the conductivity of Zr-rich PZT (95/5 Zr/Ti ratio) has been investigated., In the paraelectric region (T>520 K) the effect of the conductivity, probably due to oxygen vacancies becomes predominant at low frequencies. At the ferro-paraelectric transition temperature, T_{FP}, a straightforward analysis of the frequency dependence of the dielectric losses peak allows the characterization of the intrinsic relaxation time temperature dependence in the vicinity of the transition temperature.

Zr-rich PZT presents, in addition to the cubic-rhombohedral phase transition between the paraelectric (P_C) and the high temperature ferroelectric (F_{RH}) phases, another rhombohedral-rhombohedral transition to a low temperature ferroelectric (F_{RL}) phase which takes place at temperatures relatively close to room temperature[1], depending on the composition[2]. It makes this material attractive for specific applications[3].

The dissipation factor ($D = tan\ \delta = \varepsilon''/\varepsilon'$) is an important parameter of the material which is convenient to keep as low as possible for practical reasons. The imaginary part of the measured dielectric constant (ε'') contains two contributions: pure dielectric losses (ε''_{dip}), and an additive term due to conductivity (σ). An investigation of the frequency dependence of dielectric losses in a wide

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temperature range is useful to characterize the relaxation peak at the phase transition as well as the activation energy governing the conductivity in the various phases of a material. In this work we analyze dielectric data in a wide temperature range for Nb doped PZT, $Pb(Zr_{0.95}Ti_{0.05})O_3$, to obtain basic information on the conductivity and the relaxation behavior at the phase transitions. Nb doping is well known to increase the resistivity[4].

Ceramic samples of the above mentioned composition, PZT (95/5), were prepared at 1340 °C for 1.5 hour, in the form of disks with thickness 1.1 mm and diameter 1.5 cm, which were electroded with silver paint.

Measurements of dielectric constant and losses factor were performed at a heating rate of 20°C/h in the range 300-600 K by means of an automatic HP-LCR Meter (model 4284 A). Measurements under an a.c. field of 10 V/cm were made at 1 kHz and at 10 kHz intervals between 10 kHz and 100 kHz. The temperature was observed by means of a Keithley 196 DMM digital multimeter.

It is well known[5] that the imaginary part of the observed dielectric constant in the presence of conductivity, σ, is given by:

$$\varepsilon''_{tot} = \varepsilon''_{dip} + \frac{4\pi\sigma}{\omega} \qquad \text{(cgs-esu units)} \qquad [1]$$

where ε''_{dip} represents the dipolar contribution to the dielectric losses and $\omega = 2\pi f$ is the angular frequency.

Fig. 1 gives a semilog plot of $\varepsilon'' = \varepsilon' \tan\delta$ as a function of $1000/T$(K) for the set of frequencies specified. The two pronounced peaks in $\varepsilon''(T)$ for each frequency occur at the two transition temperatures $T_{FP}(P_C \rightarrow F_{RH}) \cong 517$ K ($\cong$ 244 °C) and $T_{LH}(F_{RH} \rightarrow F_{RL}) \cong 339$ K ($\cong$ 66 °C), respectively.

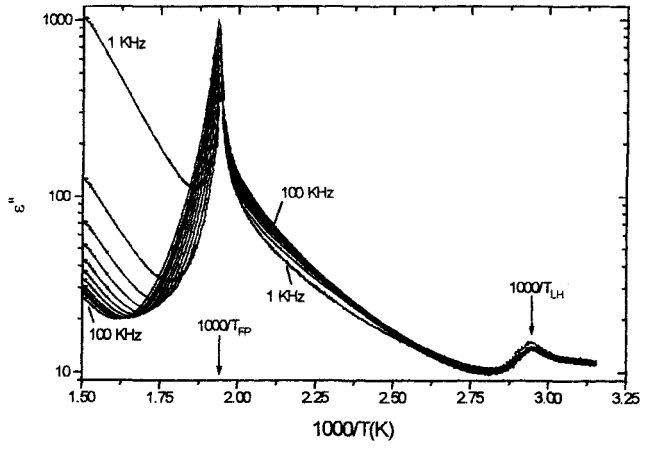

FIGURE 1. ε'' *vs.* $1000/T$ in semilog scale for Nb doped PZT (95/5)

In the paraelectric phase ($T>T_{FP}$) the measured values for ε'' at any given temperature show a pronounced frequency dependence due to large contributions from conductivity at the lower measured frequencies, being ε'' higher at the lowest frequency of 1 kHz. In the high temperature ferroelectric phase ($T_{LH}<T<T_{FP}$) the contributions from conductivity are lower, the frequency dependence of ε'' is much smaller, being ε'' now lower at the lowest frequencies, contrary to what happens in the paraelectric phase. This is likely due to a dipolar contribution to ε'' which, in the ferroelectric phase and away from the phase transition peak, is superimposed to the conductivity contribution and has a weaker frequency dependence.

We first determine a residual value of $\varepsilon'(f\to\infty)$ from plots of ε'' *vs.* $1/f$ and extrapolating to $(1/f)\to 0$. The result is $\varepsilon''_{res}\cong 7$ for $T>T_{FP}$ and $\varepsilon''_{res}<9$ for $T<T_{FP}$.

We can replot the data on $\varepsilon''(T)$ at various frequencies as $Ln[\omega(\varepsilon''-\varepsilon''_{res})/4\pi] \approx Ln[\omega\varepsilon''_{dip}(\omega,T)/4\pi + \sigma(T)]$ *vs.* $1000/T$ to get the temperature dependence of the effective conductivity, as shown in Fig. 2, where the curve for 1 kHz defines fairly well the behavior of the conductivity.

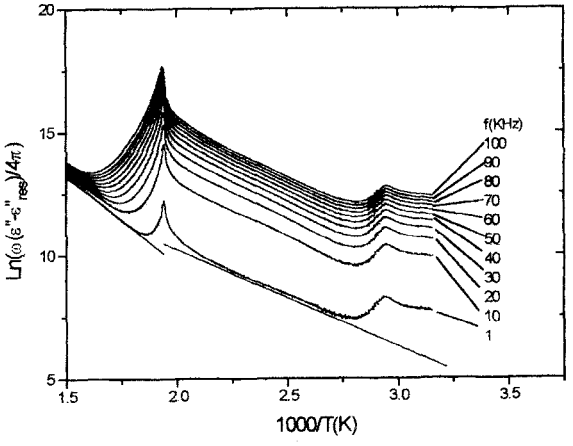

FIGURE 2. Effective conductivity $\sigma=Ln[\omega(\varepsilon''-\varepsilon''_{res})/4\pi]$ *vs.* $1000/T$(K)

The conductivity[5] for moving positive or negative ions is given by

$$\sigma(T) \cong \frac{n}{N}\frac{e^2 v}{6ak_B T}e^{-\Delta U/k_B T} \qquad [2]$$

where n/N is the ratio of the number of charge carriers to normal lattice sites, e is the carrier charge, a is the distance between neighboring potential minima in the lattice, k_B is Boltzmann's constant and ΔU the energy barrier between neighboring minima.

On the other hand conductivity for holes or electrons is given, in analogous way by

$$\sigma(T) \cong \left(ne^{-\Delta U / k_B T}\right) \frac{e^2 \tau_h}{m} \qquad [3]$$

where τ_h is the characteristic hoping time between neighboring sites and m the effective mass of the carrier. This expression for $\sigma(T)$ can be rewritten as

$$\sigma(T) \cong \frac{n}{Na^3} \frac{e^2 (v\tau_h)^2}{m v^2 \tau_h} e^{-\Delta U / k_B T} \qquad [4]$$

taking into account that $v\tau \cong a$, $1/\tau \cong \nu$ and $\frac{1}{2} m v^2 \cong k_B T$, where v is the effective velocity of motion of the carrier.

We can see that Eqs.[2] and [4] are quite similar, except by an unimportant dimensionless factor.

In the paraelectric phase ($T > T_{FP}$) the tails of the higher frequency transition peaks collapse towards the 1 kHz curve defining well the conductivity with values of $(n/N) \sim 10^{-3}$ both with Eq.[2] and with Eq.[4] (using $e \cong 2 \times 4.8\ 10^{-10}$ esu, $a \cong 4 \times 10^{-8}$ cm, $\nu \sim 4.2 \times 10^{12}$, $T \cong T_{FP} \sim 666$ K) and $\Delta U \cong 0.65$ eV. This might be interpreted either as ionic conductivity due to oxygen vacancies or hole conductivity with mh comparable to that oxygen atoms.

In the ferroelectric phase, on the other hand, the picture is more complicated. Using the same $\varepsilon''_{res} \cong 7$ from the paraelectric phase we still get straight lines at $T < T_{FP}$ away from the relaxation transition peak but the lines are displaced towards higher values for higher frequencies. As pointed out above the residual value for $f \to 0$ in this phase is not constant, probably due to additional dipolar contributions to ε'' which are much less frequency dependent than the conductivity contributions.

In a ferroelectric material, with reorientable dipole moments, the contribution to the dielectric constant, as established in Eq.[1] is given by Debye's equation[5]:

$$\varepsilon^*_{dip} = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + i\omega\tau} \qquad [5]$$

where ε'_s is the static dielectric constant, ε'_∞ is the high frequency limit ($\omega \to \infty$) dielectric constant, and τ is the dipolar intrinsic relaxation time.

At temperatures close to the phase transition $\varepsilon'_s >> \varepsilon'_\infty$ for most of the ferroelectrics[6]. On the other hand, $1/\tau$ has a pronounced minimum at the transition temperature in PZT ceramics[7]. Then, for the complex dielectric constant from Eq.[5] we approximate:

$$\varepsilon''_{dip} \approx \left[\varepsilon'_s(T)\tau(T)\right]\omega \qquad (T>T_{FP}) \qquad [6]$$

Figure 3 plots $\varepsilon''_{dip}=\varepsilon''-4\pi\sigma/\omega$ *vs.* frequency (f) at $T>T_{FP}$ (paraelectric phase (a)) and $T<T_{FP}$ (ferroelectric phase (b)) for a set of temperatures. The linear behavior with frequency of ε''_{dip} is clearly seen for various temperatures. While in the paraelectric phase (a) the straight lines approach the vertical axis towards an small common residual value at temperatures away from T_c, in the ferroelectric phase (b) this is not the case, and the straight lines meet the vertical axis at much higher values even close to T_c.

According to Eq.[6] the slope of every straight line in Fig. 3 corresponding to a given temperature results in a numerical value for $[\varepsilon'_s(T)\cdot\tau(T)]$. Taking $\varepsilon'_s(T)$ at the lowest frequency (1 kHz) we get directly

$$\tau(T) = \left(d\varepsilon''_{dip}/d\omega\right)\Big/\varepsilon'_s(T) \qquad [7]$$

where $\omega=2\pi f$ is the angular frequency.

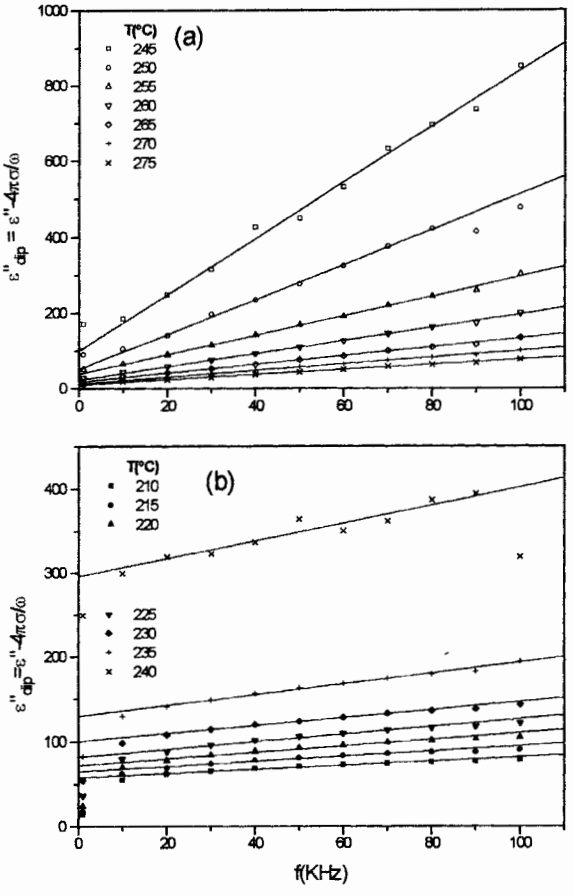

FIGURE 3. $\varepsilon''_{dip}(\omega=2\pi f)=\varepsilon''-4\pi\sigma/\omega$ *vs.* frequency (f) at various temperatures in the paraelectric (a) and ferroelectric (b) phases.

Figure 4 shows the inverse of the intrinsic relaxation time, $1/\tau$, *vs.* temperature. The behavior of $1/\tau$ with T is comparable with that found in previous

works[6,7]. At temperatures lying in the paraelectric phase ($T>T_{FP}$) a Curie law is observed, as predicted by the theory

$$\tau^{-1}(T) \cong \text{const.}\ (T - T_c) \quad , \quad T > T_{FP} \qquad [8]$$

near T_{FP}, where $T_c<T_{FP}$ is the extrapolated Curie temperature.

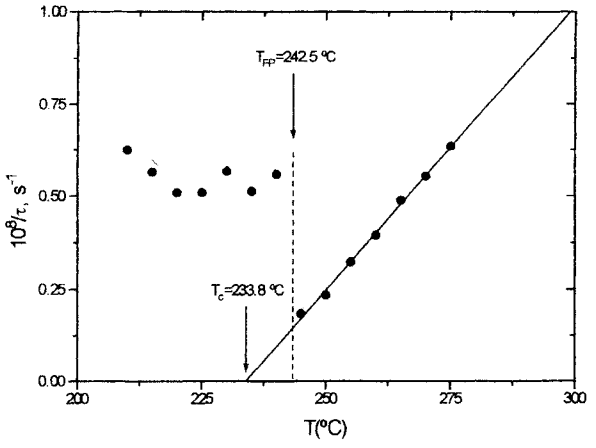

FIGURE 4. Inverse of the intrinsic relaxation time *vs.* temperature calculated from Eq.[7] and Fig. 3 (see text).

Sometimes, it is difficult to fit the Curie law at $T>T_{FP}$ for the dielectric constant due to conductivity contamination. This leads to uncertaintities in T_c of about 1°C or more. The method developed here is a complementary way to obtain both the temperature behavior of the relaxation time and the extrapolated Curie temperature (T_c).

The effect of the conductivity at high temperatures ($T>T_{FP}$) on the complex dielectric constant (ε'') has been determined. The contribution of the conductivity to ε'' was substracted in order to study the behavior of the dielectric relaxation with frequency and temperature.

Although high frequency measuring setup's (up to ~10^9 Hz) are necessary to study directly the intrinsic relaxation, at temperatures close to the phase transition $1/\tau$ decreases sufficiently to be characterized by means of relatively low frequencies (10 to 100 KHz).

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